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(54) Title: DEODORIZING AGENT FOR SULFUR- OR NITROGEN-CONTAINING INITIATORS

(57) Abstract: Cationic initiator compositions for initiating cationic polymerization which contain a sulfur- or nitrogen-containing initiator, such as a sulfonium salt photoinitiator, and a deodorizing agent are disclosed. The deodorizing agent reduces undesirable odors, such as the organosulfur/mercaptan/thio odor generated by the decomposition of the sulfonium salt initiator upon initiation. The deodorizing agent may be a free radical inhibitor or phenolic compound such as methylether of hydroquinone, toluhydroquinone and hydroquinone. Processes for making and using the composition are also disclosed. The composition has applications in the coating, photoresist, adhesion, graphic arts and sealant arts among others

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## Deodorizing agent for sulfur- or nitrogen-containing initiators

The present invention relates to sulfur- or nitrogen-containing salt initiator  
5 compositions containing a deodorizing agent which reduces undesirable odors such as  
the organosulfur/mercaptan/thio odor produced from the decomposition of sulfonium  
salt initiators. The deodorizing agent may be a free radical inhibitor or a phenolic  
compound such as, for example, hydroquinone, toluhydroquinone or methylether of  
hydroquinone. The initiator may be, for example, a sulfonium salt photoinitiator. The  
10 present invention also relates to polymerizable compositions, processes for forming the  
compositions and for its various applications in the coating, photoresist, adhesive, graphics  
and sealant arts.

There has been a long felt need to attain highly durable coatings and effective  
15 procedures which allow for the coating of substrates at high production rates while  
minimizing potential costly environmental hazards. The use of aromatic sulfonium salt  
complexes as photoinitiators in photopolymerizable formulations providing rapidly  
polymerized resin coatings have been disclosed in, for example, U.S. Patent Nos.  
3,708,296, 3,794,576, 4,058,400 and 4,058,401. The sulfonium salt photoinitiator  
20 releases cations upon exposure to actinic radiation which, in turn, initiates the cationic  
polymerization or crosslinking of one or more materials containing polymerizable or  
crosslinkable groups. These sulfonium salt photopolymerizable compositions afford many  
desirable properties and very satisfactory products. However, these compositions tend to  
emit an undesirable odor, characteristic of mercaptan and other organosulfur  
25 compounds, generated from the decomposition of the sulfonium salt initiator. The  
industry has therefore been seeking novel sulfonium salt compositions and processes  
which would not produce the undesirable odor upon cure of prior compositions.

In U.S. Patent Nos. 4,250,230 and 4,306,953, sulfonium salt photopolymerizable compositions are disclosed which include a scavenger or stable free radical to reduce the sulfur odor emitted by the photodecomposed sulfonium salt.

5 However, the disclosed additives provide a negative effect on the cure rates, adhesion and MEK rub resistance.

US Patent No. 4,324,679 discloses sulfonium salt photopolymerizable systems containing an aromatic radical additive which provides odor reduction. However, there is no disclosure of phenolic compounds or free radical inhibitors as the additive, nor does  
10 US 4,324,679 disclose the effects on the additive on any of the physical properties of the curing composition.

US Patent N° 4,218,531 describes epoxy resins cured by sulfonium salts. The starting composition contains an additive minimizing or eliminating the odor of organosulfur reaction by-products. This additive must contain non-aromatic carbon-carbon, ethylenic  
15 unsaturation. An ethylenic unsaturation is susceptible to oxidative crosslinking by oxygen insertion into the unsaturated group, followed by thermal cleavage of the resulting peroxide to generate radicals, which crosslink with adjacent molecules. Therefore the additives described in US N° 4,218,531 can not be considered as free radical inhibitors. There is no mention of the presence of a phenolic group (hydroxy directly bonded to an  
20 aromatic moiety) in the additive.

US patent N°4,250,203 describes photopolymerizable compositions containing sulfonium salts initiators and an organic sulfur compound scavenger. The scavenger compounds described are a series of ketone and ketone-like compounds. In no case is a phenolic compound described. Most of the scavenger compounds described in this patent  
25 are specifically described as free radical initiators in J. Sanchez and T. N. Meyers, in J. I. Kroschwitz, ed., "Initiators (Free Radical)", pps 431-460, in *Encyclopedia of Chemical Technology*, Vol. 14, 4<sup>th</sup> edition, Wiley-Interscience, New York, 1992.

Therefore, none of the prior art teaches nitrogen- or sulfur-containing initiator compositions comprising a deodorizing agent in the form of a phenolic compound or free radical inhibitor which does not severely compromise the curing rates and other physical properties of the composition.

5

It is an object of the present invention to provide a novel cationic initiator composition for initiating cationic polymerization comprising a sulfur- or nitrogen-containing initiator, such as, for example, a sulfonium salt photoinitiator, and a deodorizing agent which reduces the odor of the photoinitiator composition upon  
10 initiation due to the decomposition of the a sulfur- or nitrogen-containing photoinitiator.

It is also an object of the present invention to provide a curable cationic polymerizable composition comprising a sulfur- or nitrogen-containing initiator, a polymerizable material, and a deodorizing agent; wherein the deodorizing agent reduces the undesirable sulfur- or nitrogen-compound odor of the composition generated upon  
15 the decomposition of the sulfur- or nitrogen-containing photoinitiator during initiation. In a preferred embodiment, the initiator is a sulfonium salt photoinitiator whereas the deodorizing agent is a phenolic compound or free radical inhibitor which does not compromise the curing rate, MEK rub resistance and other physical properties of the composition.

20

A further object of the present invention is to provide a process for curing a cationic polymerizable composition containing a sulfur- or nitrogen-containing initiator, such as, for example, a sulfonium salt photoinitiator, and polymerizable material which comprises adding a deodorizing agent to said composition in order to reduce the odor upon curing generated by the decomposition of the sulfur- or nitrogen-containing  
25 initiator. A preferred initiator is a sulfonium salt photoinitiator and a preferred deodorizing agent is a free radical inhibitor or phenolic compound such as, for example, a

quinone or a quinone derivative. This process can be used in, for example, coating, photoresist, adhesive, graphics, and sealant applications.

Another object of the present invention is to provide positive- and negative-acting acid sensitive photoresist compositions comprising a photoactive sulfur- or nitrogen- containing compound such as, for example, a photoactive sulfonium salt, a resin binder and a deodorizing agent which reduces the odor of the compound upon initiation.

A further object of the present invention is to provide an article of manufacture having at least one surface wherein said surface comprises a coating layer of a positive- or negative-acting acid sensitive photoresist composition comprising a photoactive sulfur- or nitrogen- containing compound such as, for example, photoactive sulfonium salt, a resin binder and a deodorizing agent; wherein said deodorizing agent reduces the odor of the compound upon cure.

A final object of the present invention is to provide a process for preparing an acid sensitive photoresist composition containing a photoactive sulfur- or nitrogen- containing compound such as, for example, photoactive sulfonium salt and a resin binder; wherein the improvement comprises adding a deodorizing agent to said acid sensitive photoresist composition in order to reduce the odor attained upon curing due to the photo-decomposition of the sulfonium salt photoinitiator.

20

The present invention relates to cationic initiator compositions for initiating cationic polymerization comprising a sulfur- or nitrogen-containing initiator and a deodorizing agent; wherein the deodorizing agent reduces the odor of the initiator composition upon initiation due to the decomposition of the nitrogen or sulfur-containing- compound initiator such as, for example, a sulfonium salt photoinitiator.

25

Particularly, formulations containing sulfur-containing initiators, especially sulfonium salt initiators develop an unpleasant organosulfur/mercaptan/thio odor upon cure. Cure is typically initiated by actinic radiation, but these initiator compositions can also be activated by ionizing irradiation or by heat. Applicant has found that the odor  
5 generated by these formulations may be reduced upon addition of certain additives such as phenolic compounds or free radical inhibitors. These initiator compositions have applications in the coating, photoresist, adhesion, ink and sealant arts.

In a preferred embodiment, the sulfur- containing initiator is a sulfonium salt photoinitiator, whereas the deodorizing agent is a free radical inhibitor or phenolic  
10 compound, such as a quinone or a quinone derivative, which does not compromise the curing rate, MEK resistance and/or other physical properties of the composition.

A "free radical inhibitor" is a compound added to a radically polymerizable composition to inhibit or prevent radical polymerization.

Other synonyms for "free radical inhibitor" include polymerization inhibitor,  
15 stabilizer, antioxidant, radical scavenger:

Polymerization inhibitors are additives which slow or inhibit the polymerization process. Stabilizers are additives which stabilize a formulation, that is which prevent cure or degradation of a formulation in the can, and allow it to be stored for a long period of time (up to several months or longer) before use.

20 Antioxidants prevent the reduction of organic materials with atmospheric oxygen to form hydroperoxides, which cleave easily to yield radicals. Antioxidant compounds which prevent this process, especially when used as additives to ethynically unsaturated oligomers and oligomers, are commonly called free radical inhibitors (M. Dexter, in J. I. Kroschwitz, ed., "Antioxidants", pps 424-447, in *Encyclopedia of Chemical Technology*,  
25 Vol. 3, 4<sup>th</sup> edition, Wiley-Interscience, New York, 1992).

Radical scavengers compete with the organic substrate for peroxy radicals, forming stable radicals which are not reactive with the substrate.

A number of radical inhibitors are known in the art, following are some examples  
5 taken from R. Holman, P. Oldring, p. 22 in *U.V. and E.B. Curing Formulations for Printing Inks, Coatings and Paints*, SITA-Technology, London, 1988, the content of which being incorporated herein by reference:

- Hydroquinone
- Methoxy methyl hydroquinone
- 10 ▪ p-benzoquinone
- phenothiazine
- mono-tert-butyl quinone
- catechol
- p-tert-butyl catechol
- 15 ▪ Benzoquinone
- 2, 5 di tert-butyl hydroquinone
- 2, 5 p-dimethyl p-benzoquinone
- Anthraquinone
- 2, 6 di-tert-butyl hydroxy toluene.

20

Other suitable free radical inhibitors are mentioned on Table 4 of M. Dexter, in J. I. Kroschwitz, ed., "Antioxidants", pps 424-447, in *Encyclopedia of Chemical Technology*, Vol. 3, 4<sup>th</sup> edition, Wiley-Interscience, New York, 1992, the content of which being incorporated herein by reference:

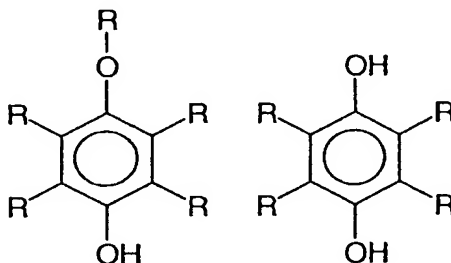
- monophenols, for example those with CAS registry numbers: 128-39-2, 128-37-0, 4130-42-1, 4306-88-1, 1879-09-0, 110553-27-0, 61788-44-1, 17540-75-9, 2082-79-3, 103-99-1, 88-27-7, 991-84-4,
- diphenols for example those with CAS registry numbers: 119-47-1, 88-24-4, 118-82-1, 35958-30-6, 36443-68-2, 85-60-9, 96-69-5, 96-66-2, 35074-77-2, 41484-35-9, 23128-74-7, 65140-91-2, 30947-30-9, 70331-94-1, 32687-78-8, 32509-66-3, 105350-68-3
- polyphenols for example those with CAS registry numbers: 68610-51-5, 6683-19-8, 1709-70-2, 27676-62-6, 1843-03-4, 34137-09-2, 40601-76-1
- hydroquinons for example those with CAS registry numbers 79-74-3, 1948-33-0, 121-00-6
- diarylamines for example those with CAS registry numbers: 90-30-2, 68442-68-2, 68259-36-9, 101-67-7, 10081-67-1
- alkylated p-phenylenediamines for example those with CAS registry numbers: 793-24-8, 101-72-4, 69796-47-0, 15233-47-3, 101-87-1, 74-31-7, 93-46-9, 3081-14-9, 139-60-6, 793-24-8, 103-96-8, 100-93-6,
- dihydroquinolines for example those with CAS registry numbers: 26780-96-1, 89-28-1, 91-53-2,
- thioethers for example those with CAS registry numbers: 2500-88-1, 123-28-4, 693-36-7, 16545-54-3, 10595-72-9, 29598-76-3, 53988-10-6, 61617-00-3, 26523-78-4, 26741-53-7, 3806-34-6, 31570-04-4, 38613-77-3, 118337-09-0,
- hindered amines for example those with CAS registry numbers: 70624-18-9, 82541-48-7, 106990-43-6.

Applicant has found that formulations comprising epoxy resin, a sulfonium salt photoinitiator and phenolic compounds such as methyl ester of hydroquinone



(MEHQ), have remarkably little odor after cure when compared to similar epoxy formulations without the added phenolic compounds. Addition of phenolic inhibitors such as MEHQ produce little or no color development over several weeks at room temperature, nor do they affect formulation cure speeds or the cured properties. Thus the addition of a deodorizing agent such as a phenolic inhibitor as, for example, MEHQ, can produce a unique and improved product which distinguishes the initiator of the present invention from initiators of the prior art. Reduction of the undesirable organosulfur/mercaptan/thio odor produced by sulfonium salt initiators during and after cure would be invaluable for production scale curing of these compositions.

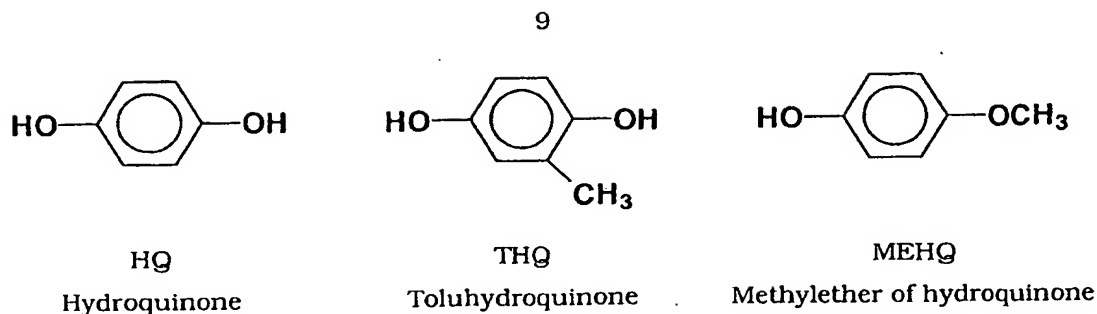
Among the additives, free radical inhibitors and phenolic inhibitors which can serve as the deodorizing agent in the present invention are quinones and their derivatives. These quinone derivatives have the following structure:



wherein the "R" substituents may be, independently, for example, C1-C20 linear or branched aliphatic alkyl groups, or cycloaliphatic groups or aromatic groups, which may eventually themselves be substituted with functional groups such as ester, hydroxy, nitrile, carboxy, halogen etc.

Among suitable quinone derivatives are the following:

Inhibitors Tested:

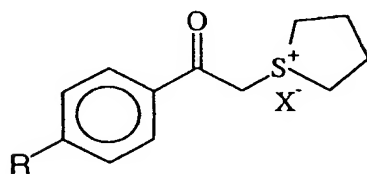
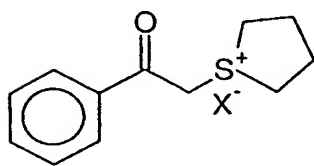
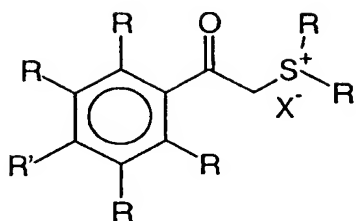


In particular, methylether of hydroquinone (MEHQ), when added to sulfonium salt initiator solutions, produces little or no color development and furthermore is very easy to incorporate in initiator solutions. In fact, addition of up to 1500 or more ppm of MEHQ (based on the total curable composition) to the sulfonium salt initiator does not affect formulation cure speeds or cured properties. It has been found that the addition of MEHQ to the sulfonium salt initiator formulation results in an unexpected improvement and reduction in the organosulfur/mercaptan/thio odor released upon the decomposition of the sulfonium salt initiator which develops during cure. Consequently, curing at large scales will amplify this effect.

Among the initiators which may be used are sulfonium salt initiators, wherein the sulfonium salt is selected from among dialkylphenacylsulfonium salts, dialkyl-4-hydroxyphenylsulfonium salts, bis-p-diphenylsulfoniumphenylsulfide salts, diphenylphenylthiophenyl sulfonium salts, benzylsulfonium salts, benzyltetramethylene sulfonium salts, benzyl(p-hydroxyphenyl)methyl-sulfonium salts, triarylsulfonium salts, triphenylsulfonium salts and mixtures thereof. The sulfonium salt initiators may contain arylsulfonium salts as major components with possibly other sulfonium salts present in low concentrations as shown below.

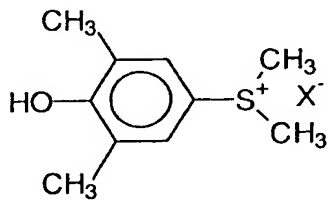
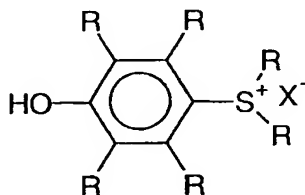
Examples of these sulfonium salt initiators include the following dialkylphenacylsulfonium salts; wherein if several R's are indicated, the R's may be the same or different; and wherein the X<sup>-</sup> may be any anion as described below:

10

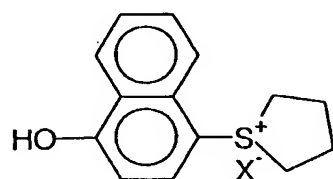
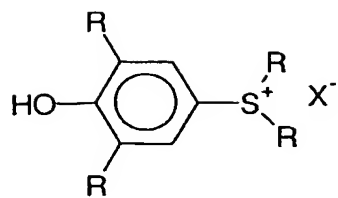


Other examples of the sulfonium salt include the following dialkyl-4-

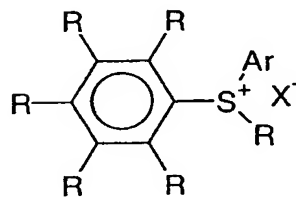
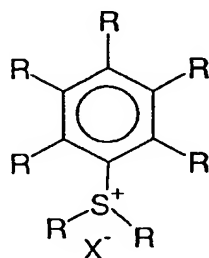
5 hydroxyphenylsulfonium salts:



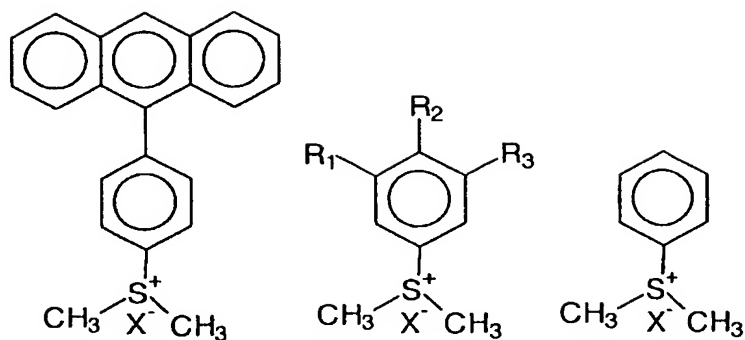
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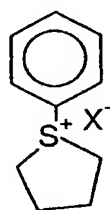
Among preferred benzylsulfonium salts are the following:



12

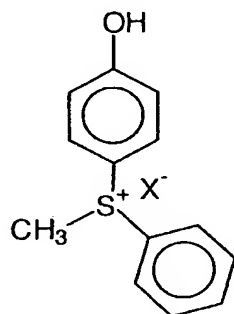


Other preferred benzyl salts include the following:



5

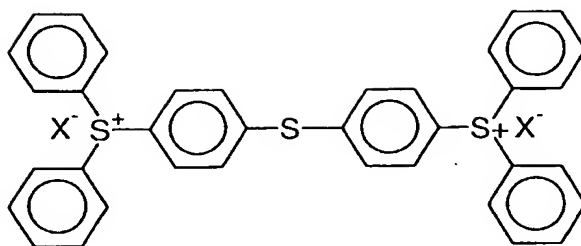
benzyltetramethylenesulfonium salts



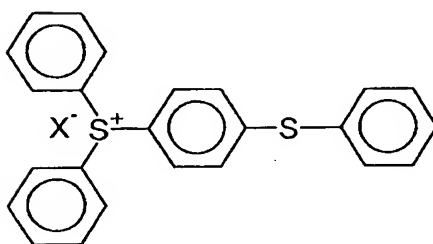
benzyl(p-hydroxyphenyl)methyl-sulfonium salts

Also, the sulfonium salt initiator may be selected from the following:

13

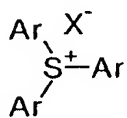


bis-p-diphenylsulfoniumphenylsulfide salts

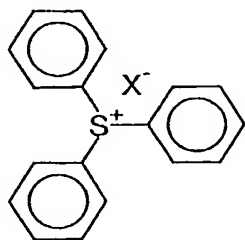


diphenylphenylthiophenylsulfonium salts

- 5            Regarding the triarylsulfonium salts, these may be commercial initiators but in the present invention the aryl group can be any aromatic group such as phenyl, naphthyl, cumyl, and tolyl, etc.



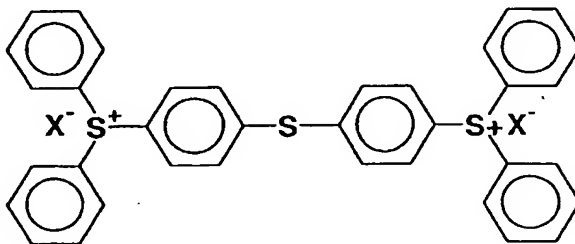
Triarylsulfonium salts



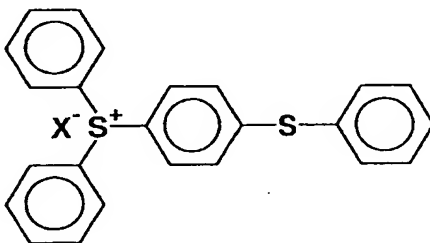
Triphenylsulfonium salts

10

Many commercial sulfonium salt initiators typically contain a blend of the following two molecules (plus small amounts of other compounds):

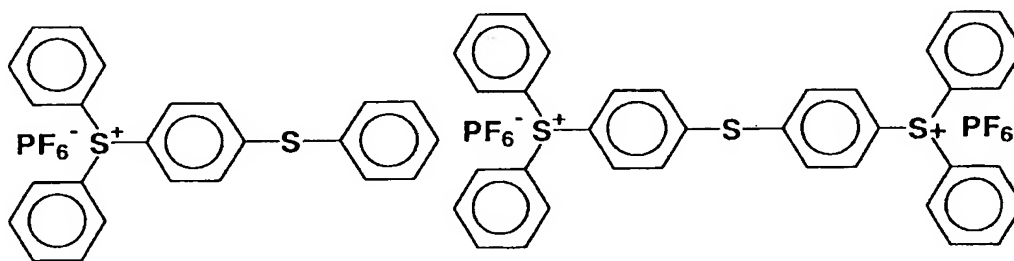


Bis-p-diphenylsulfoniumphenylsulfide salt



Diphenylphenylthiophenylsulfonium salt

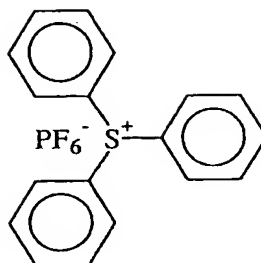
For example, commercial "Triarylsulfonium Hexafluorophosphate" initiators contain the following major components although other sulfonium salts may be present in low concentrations:



"Mixed Triarylsulfonium Hexafluorophosphate"

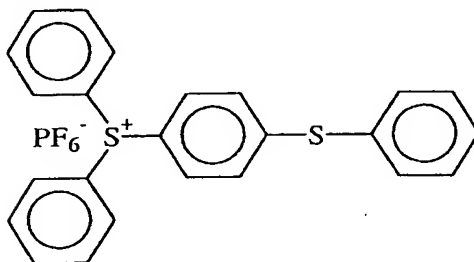
Besides those discussed above, other triarylsulfonium salts which can be used as initiators are:

15



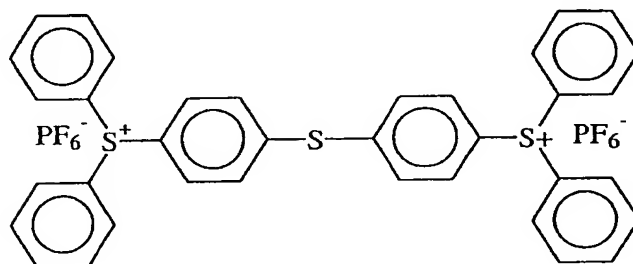
CAS # 57835-99-1

Triphenylsulfonium Hexafluorophosphate

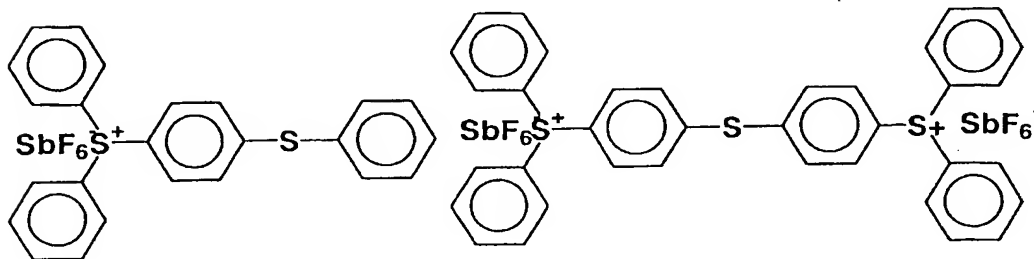


CAS # 68156-13-8

Diphenylphenylthiophenylsulfonium Hexafluorophosphate



CAS # 74227-35-3

Bis-*p*-diphenylsulfoniumphenylsulfide Hexafluorophosphate

10



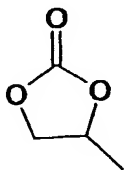
"Triarylsulfonium Hexafluoroantimonate"

A number of other sulfonium compounds (cations) may also be present in small amounts. The distribution and products are a result of the synthetic process used to make the sulfonium salts. (See e.g., US 2,807,648 for a discussion of the process of making triaryl sulfonium compounds).

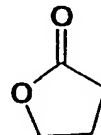
The counterions (anions) can be selected from a large number of organic and inorganic anions. Counterions (anions) may be non-nucleophilic "complex metal halide anions" such as  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$  or anions of strong protonic acids such as  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{FSO}_3^-$ ,  $\text{CH}_3\text{SO}_3^-$ , or  $\text{C}_4\text{F}_9\text{SO}_3^-$ . Counteranions may also include fluoroorganic imide or methide anions as are described in US 5,554,664. The counterion may be any other non-nucleophilic anion, such as borates or gallates, such as are  $\text{B}(\text{C}_6\text{F}_5)_4^-$ ,  $\text{Ga}(\text{C}_6\text{F}_5)_4^-$ ,  $\text{B}(\text{C}_6\text{H}_5)_4^-$ ,  $\text{B}[\text{C}_6\text{H}_2(\text{CF}_3)_3]_4^-$  or  $\text{B}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4^-$ .

The cationic initiator composition for initiating cationic polymerization may further comprise a solvent, wherein the solvent may be, for example, propylene carbonate, butyrolactone, tetrahydrofuran, *N,N*-dimethylformamide, alcohols such as aliphatic and aromatic alcohols, ethers, aromatic hydrocarbons, cyclic ethers, aliphatic hydrocarbons, benzene, toluene, dioxane, tetrahydropyran, dimethoxyethane, *n*-hexane, cyclohexane, acetone, acetonitrile or mixtures thereof.

Among the preferred solvents are propylene carbonate and  $\gamma$ -butyrolactone:



Propylene Carbonate

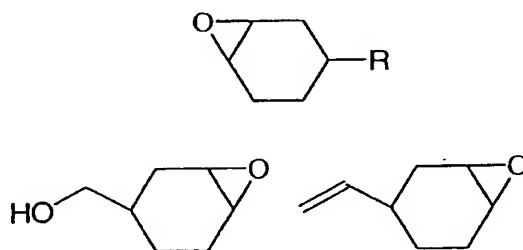


$\gamma$ -Butyrolactone  
(Dihydro-2(3H)-furanone)

Among the polymerizable materials which can be used with the present invention are epoxy resins, including cycloaliphatic epoxides, diepoxides and polyepoxides, epoxy oligomers and diglycidyl ethers, acrylate oligomers and mixtures thereof. Also, the polymerizable material can further be chosen from among glycidyl  
 5 ethers, polyorganosiloxanes, epoxypolyorganosiloxanes, vinyloxysubstituted polyorganosiloxanes, oxetanes and other cyclic ethers, vinyl ethers, alpha olefins, dienes, butadienes, isoprene, natural oils, castor oil, linseed oil, styrenes, alpha methyl styrenes, vinyl toluenes, phenyl vinyl ethers, N-vinyl carbazole, N-vinyl pyrrolidinones, acid curable materials and mixtures thereof.

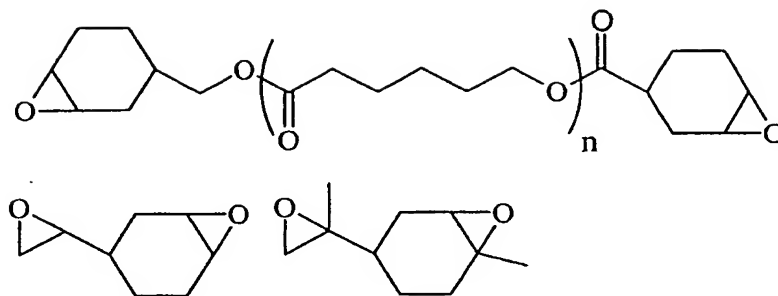
10 Furthermore, the polymerizable materials which can be used with the present invention include glycidyl ether moieties selected from diglycidyl ethers of bisphenol A, diglycidyl ethers of bisphenol F, epoxy phenol novolacs, epoxy cresol novolacs, bisphenol A epoxy novolacs, tetraglycidyl ether of tetrakis(4-hydroxyphenyl)ethane, glycidyl ethers of the condensation product of dicyclopentadiene and phenol, triglycidyl ether of  
 15 tris(hydroxyphenyl)methane and mixtures thereof.

Epoxy resins which may be used with the present invention include:



cycloaliphatic epoxides

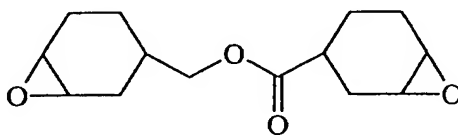
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cycloaliphatic diepoxides

5

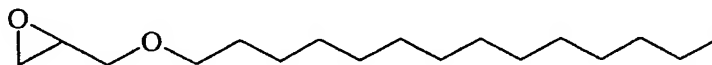
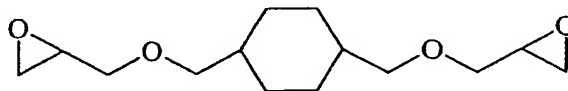
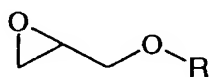
For example, a preferred cycloaliphatic diepoxide which can be used with the present invention is:



3,4-Epoxy-1-methylcyclohexyl 3,4-epoxycyclohexanecarboxylate or "EEC"

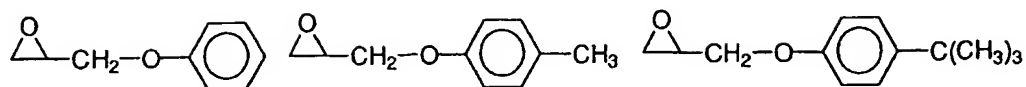
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Examples of glycidyl ether monomers which can be used with the present invention are:



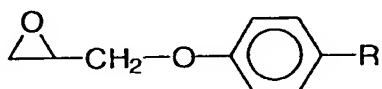
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## aliphatic glycidyl ethers

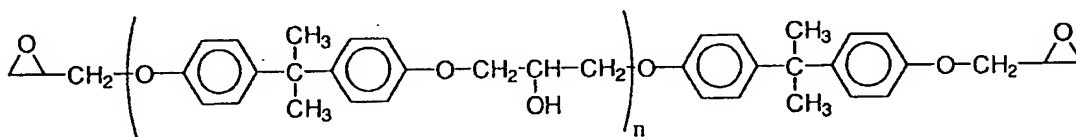


## aromatic glycidyl ethers

- Aromatic glycidyl ether resins that are suitable for the present invention are  
 5 based on the following structure where R can be almost any aliphatic or aromatic group:

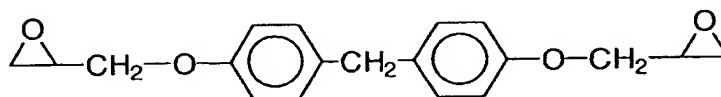


Examples of specific aromatic glycidyl ether resins which can be used in the present invention include:



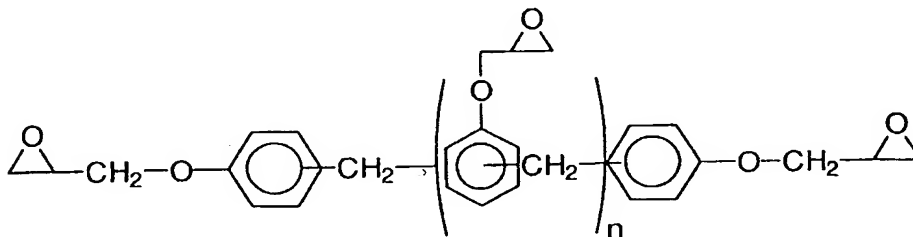
10

## diglycidyl ethers of bisphenol A



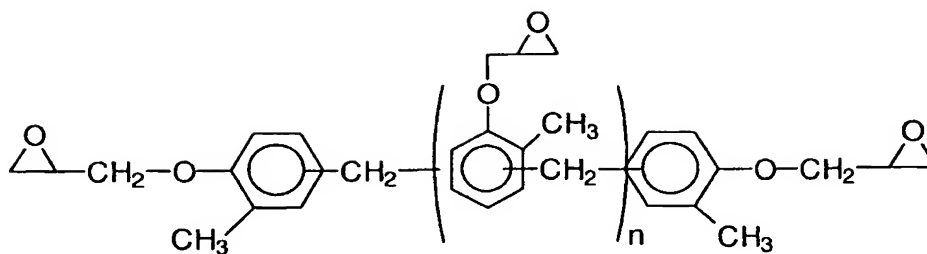
## diglycidyl ethers of bisphenol F

Among the epoxy novolacs that may be used in the present invention are:

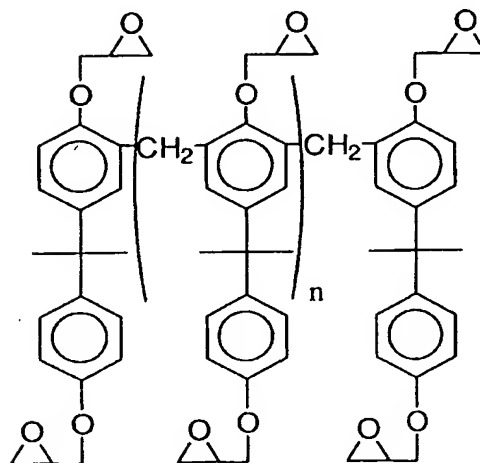


15

## epoxy phenol novolacs



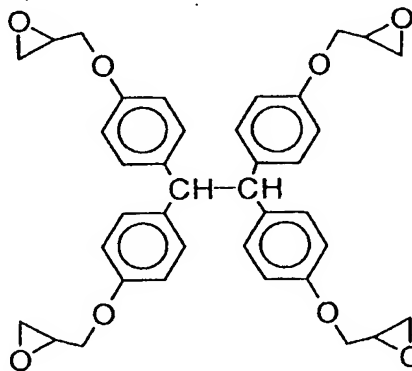
epoxy cresol novolacs



bisphenol A epoxy novolacs

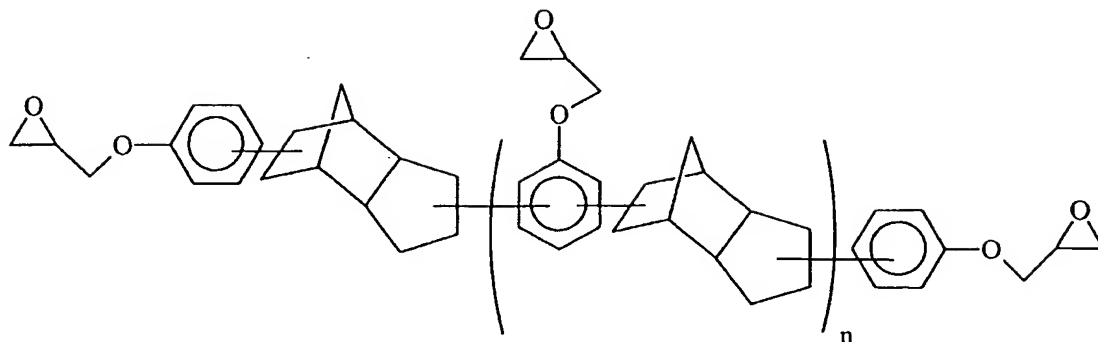
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Also, the following glycidyl ethers may be used in the present invention:

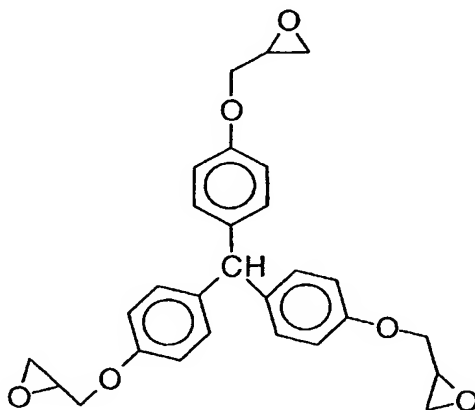


tetraglycidyl ether of tetrakis(4-hydroxyphenyl)ethane

21

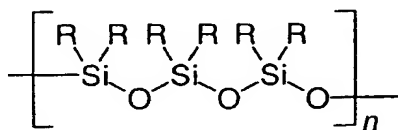


glycidyl ethers of the condensation product of dicyclopentadiene and phenol



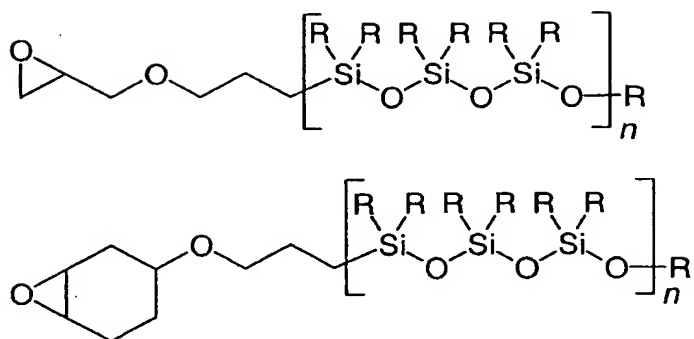
triglycidyl ether of tris(hydroxyphenyl)methane

- 5 The following polyorganosiloxanes may also be used as the polymerizable material in the present invention, wherein R is typically a methyl group, but instead can also be ethyl, phenyl, or any aliphatic group. In other instances, R could also be an epoxy or other reactive group. If several R's are indicated, the R's may be the same or different.

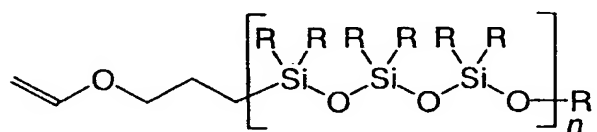


polyorganosiloxanes

22



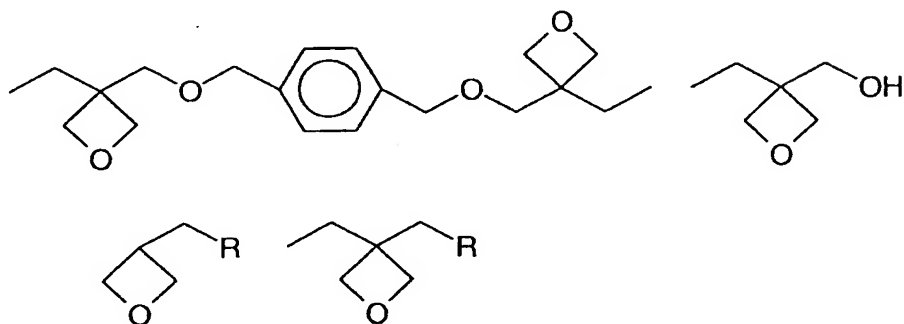
epoxypolyorganosiloxanes



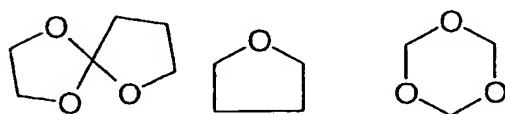
vinylloxysubstituted polyorganosiloxanes

5

Other examples of the polymerizable material which may be used in the present invention are the following oxetanes, cyclic ethers and vinyl ethers.



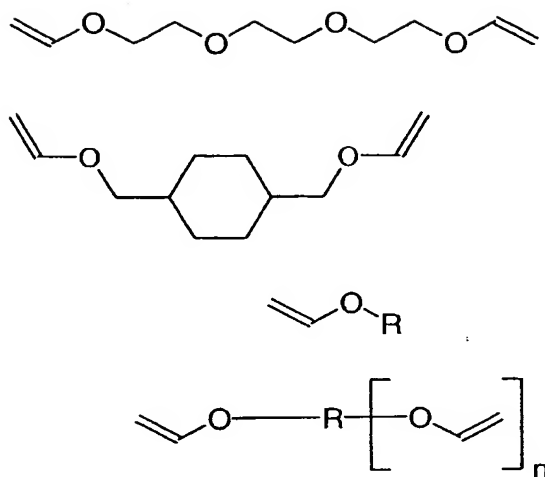
oxetanes



cyclic ethers

10

23



vinyl ethers

5

There are also provided curable cationic polymerizable compositions comprising a sulfur- or nitrogen-containing initiator, polymerizable material, and a deodorizing agent; wherein the deodorizing agent reduces the sulfur- or nitrogen-compound odor of the composition upon initiation. A preferred class of initiators are sulfonium salt initiators.

10 A more preferred class of initiators are sulfonium salt photoinitiators.

This curable composition can be cured by radiation or irradiation such as, for example, actinic, ultraviolet, visible light, infrared, microwaves, radio, ionizing, alpha, beta, gamma, X-rays or electron beams.

The polymerizable material can be selected from among epoxy monomers, epoxy  
15 oligomers, acrylate oligomers and mixtures thereof, including all of the polymerizable materials described earlier.

For example, the polymerizable material can be chosen from among aromatic epoxy resins, aliphatic epoxy resins, cycloaliphatic epoxide, diepoxide and polyepoxide resins, glycidyl ethers, polyorganosiloxanes, epoxypolyorganosiloxanes,  
20 vinyloxysubstituted polyorganosiloxanes, oxetanes and other cyclic ethers, vinyl ethers, alpha olefins, dienes, butadienes, isoprene, natural oils, castor oil, linseed oil, styrenes,



alpha methyl styrenes, vinyl toluenes, phenyl vinyl ethers, N-vinyl carbazole, N-vinyl pyrrolidinones, acid curable materials and mixtures thereof.

Furthermore, the cationic polymerizable composition can comprise polymerizable material such as epoxy resin moieties selected from among diglycidyl ethers of bisphenol A, diglycidyl ethers of bisphenol F, epoxy phenol novolacs, epoxy cresol novolacs, bisphenol A epoxy novolacs, tetraglycidyl ether of tetrakis(4-hydroxyphenyl)ethane, glycidyl ethers of the condensation product of dicyclopentadiene and phenol, triglycidyl ether of tris(hydroxyphenyl)methane and mixtures thereof.

The deodorizing agent can be a free radical or phenolic compound. The phenolic compound can be a quinone or a quinone derivative such as hydroquinone, toluhydroquinone, or methylether of hydroquinone.

Preferred sulfur-containing initiators are sulfonium salt photoinitiators containing the sulfonium salts discussed above. For example, the sulfonium salt can be selected from among dialkylphenacylsulfonium salts, dialkyl-4-hydroxyphenylsulfonium salts, bis-p-diphenylsulfoniumphenylsulfide salts, diphenylphenylthiophenyl sulfonium salts, benzylsulfonium salts, benzytetramethylene sulfonium salts, benzyl(p-hydroxyphenyl)methyl-sulfonium salts, triarylsulfonium salts, triphenylsulfonium salts and mixtures thereof.

The counterions (anions) can be selected from a large number of organic and inorganic anions, as described previously. Counterions (anions) may be non-nucleophilic "complex metal halide anions" such as  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$  or anions of strong protonic acids such as  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{FSO}_3^-$ ,  $\text{CH}_3\text{SO}_3^-$  or  $\text{C}_4\text{F}_9\text{SO}_3^-$ . Counteranions may also include fluoroorganic imide or methide anions as are described in US 5,554,664. The counterion may be any other non-nucleophilic anion, such as borates or gallates such as are  $\text{B}(\text{C}_6\text{F}_5)_4^-$ ,  $\text{Ga}(\text{C}_6\text{F}_5)_4^-$ ,  $\text{B}(\text{C}_6\text{H}_5)_4^-$ ,  $\text{B}[\text{C}_6\text{H}_2(\text{CF}_3)_3]_4^-$  or  $\text{B}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4^-$ .

In addition, the curable composition may further comprise a solvent selected from among propylene carbonate, butyrolactone, tetrahydrofuran, *N,N*-dimethylformamide, alcohols, ethers, aromatic hydrocarbons, cyclic ethers, aliphatic hydrocarbons, benzene, toluene, dioxane, tetrahydropyran, dimethoxyethane, n-hexane, cyclohexane, acetone, acetonitrile and mixtures thereof.

The curable composition may further comprise a reactive diluent. This reactive diluent may be selected from among epoxides such as low viscosity epoxides, diepoxides, and polyepoxides, low viscosity alcohols, polyols such as polycaprolactone triols, phenols, vinyl ethers, vinyl monomers, cyclic ethers, tetrahydrofuran, tetrahydropyran, cyclic carbonates, cyclic esters, butyrolactone, propylene carbonate, acrylates, methacrylates, aliphatic monohydric alcohols and compounds containing two or more different functional groups on one molecule.

Also, a process for curing a cationic polymerizable composition was found for a composition containing a sulfonium salt initiator in polymerizable material; wherein the improvement comprises adding a deodorizing agent to the composition in order to reduce the odor upon curing. The process includes the cationic polymerizable composition being cured by radiation or irradiation such as, for example, actinic, ultraviolet, visible light, infrared, microwaves, radio, ionizing, alpha, beta, gamma, X-rays or electron beams.

The process may comprise polymerizable material, a deodorizing agent, a sulfonium salt initiator and a reactive diluent selected from the same polymerizable materials, deodorizing agents, sulfonium salt initiators and reactive diluents discussed previously in forming the cationic initiator composition and the curable cationic polymerizable composition.

The instant initiator composition is also applicable in the photoresist art. Photoresists are photosensitive films used to transfer images to a substrate to form positive or negative images. A photoresist is coated onto a substrate followed by exposure

of the coating through a patterned photomask to an activating radiation source. A latent image pattern is defined on the photoresist coating due to opaque and transparent areas to the activating radiation in the photomask. A relief image is provided by developing the latent image pattern in the resist coating.

5           Positive acting- or negative acting-acid sensitive photoresist compositions were found which comprise a photoactive sulfur- or nitrogen-containing compound such as, for example, a photoactive sulfonium salt compound, a resin binder and a deodorizing agent; wherein the deodorizing agent may be a phenolic compound or a free radical inhibitor which reduces or eliminates the organosulfur/mercaptan/thio odor generated upon the  
10   decomposition of the sulfonium salt photoinitiator upon initiation. This composition may be a chemically amplified positive-acting photoresist or may be a negative-acting photoresist composition.

          The resin binders for the positive acting- or negative acting -photoresist composition may be selected from among novolac resins, block novolac resins, phenolic  
15   compounds, phenolic resins, vinylphenols, polyvinylphenols, partially hydrogenated derivatives of novolacs, partially hydrogenated derivatives of phenolic compounds, copolymers containing phenolic moieties, copolymers containing aliphatic cyclic alcohol moieties, bishydroxymethylated compounds comprising polar functional groups, compounds comprising hydroxyl groups, compounds comprising carboxylate groups,  
20   imide polymers, styrenes, styrene copolymers, vinylic polymers, polyolefins and mixtures thereof.

          The positive- or negative-acid sensitive photoresist composition may further include a crosslinker. The crosslinker can be selected from among amines, melamines, glycolurils, benzoguanamines, ureas, melamine-formaldehyde resins and mixtures  
25   thereof.

The positive acting- or negative acting-acid sensitive photoresist composition can further include additives. These additives can be selected from the group consisting of actinic dyes, contrast dyes, anti-striation agents, plasticizers, speed enhancers and photosensitizer compounds.

5           The positive acting- or negative acting-acid sensitive photoresist composition can be cured by radiation or irradiation selected from among actinic, ultraviolet, visible light, infrared, microwaves, radio, ionizing, alpha, beta, gamma, X-rays and electron beams.

          The deodorizing agent can be a free radical inhibitor or a phenolic  
10   compound. The phenolic compound may be a quinone or a quinone derivative such as, for example, hydroquinone, toluhydroquinone and methylether of hydroquinone.

          The photoactive sulfonium salt may be a sulfonium salt. The sulfonium salt can be chosen from among dialkylphenacylsulfonium salts, dialkyl-4-  
hydroxyphenylsulfonium salts, bis-p-diphenylsulfoniumphenylsulfide salts,  
15   diphenylphenylthiophenyl sulfonium-salts, benzylsulfonium salts, benzyltetramethylene sulfonium salts, benzyl(p-hydroxyphenyl)methyl-sulfonium salts, triarylsulfonium salts, triphenylsulfonium salts and mixtures thereof.

          The positive acting- or negative acting-acid sensitive photoresist composition may further include a solvent wherein said solvent may be selected from propylene  
20   carbonate, butyrolactone, tetrahydrofuran, *N,N*-dimethylformamide, alcohols such as aliphatic and aromatic alcohols, ethers, aromatic hydrocarbons, cyclic ethers, aliphatic hydrocarbons, benzene toluene, dioxane, tetrahydropyran, dimethoxyethane, n-hexane, cyclohexane, acetone, acetonitrile and mixtures thereof.

          The acid sensitive photoresist composition can be applied as a coating layer of  
25   an article of manufacture having at least one surface. Conventional methods known in

the art such as coating, extrusion and lamination may be used to apply the photoresist layer on to the article surface.

In addition, the present invention includes a process for preparing the positive- or negative acting- acid sensitive photoresist compositions containing a photoactive sulfur- or nitrogen- containing compound such as, for example, a photoactive sulfonium salt in the resin binder; wherein the improvement comprises adding a deodorizing agent to the acid sensitive photoresist composition in order to reduce the odor generated by decomposition of the sulfonium salt photoinitiator upon curing.

The following examples further illustrate the best mode contemplated by the inventors for the practice of their invention. The examples are to be construed as illustrative of and not in limitation of the invention.

With respect to the materials employed in the following working examples, the following information is provided:

Abbreviation	Commercial Source	Composition
Cyracure UVI-6990, UVI-6990	Union Carbide	50% Mixed triarylsulfonium salts having PF <sub>6</sub> <sup>-</sup> as counterion in 50% Propylene carbonate
FX-512	3M Product	45-55% Mixed triarylsulfonium salts having PF <sub>6</sub> <sup>-</sup> as counterion in 40% $\gamma$ -Butyrolactone
Uvacure 1590	UCB	50% Mixed triarylsulfonium salts having PF <sub>6</sub> <sup>-</sup> as counterion in 50% Propylene carbonate
SarCat CD 1011	Sartomer	50% Mixed triarylsulfonium salts having PF <sub>6</sub> <sup>-</sup> as counterion in 50% Propylene carbonate
Cyracure UVI-6974, UVI-6974	Union Carbide	50% Mixed triarylsulfonium salts having SbF <sub>6</sub> <sup>-</sup> as counterion in 50% Propylene carbonate
SarCat CD 1010	Sartomer	50% Mixed triarylsulfonium salts having SbF <sub>6</sub> <sup>-</sup> as counterion in 50% Propylene carbonate
Tone 301	Union Carbide	Polycaprolactone triol
Silwet L-7602	OSi Specialties	Surfactant
EEC	UCB	3,4-Epoxy-cyclohexylmethyl-3,4-epoxy-cyclohexane carboxylate
MEHQ	Aldrich	Methylether of hydroquinone

Abbreviation	Commercial Source	Composition
HQ	Aldrich	Hydroquinone
THQ	Aldrich	Toluhydroquinone

There was tested a curable formulation containing EEC, a triaryl sulfonium hexafluorophosphate salt initiator in propylene carbonate (50 % solids) and 500 ppm MEHQ and proved that the organosulfur/mercaptan/thio odor produced by the sulfonium salt photoinitiator was reduced during and after cure.

5           Testing was performed on several phenolic compound/ sulfonium salt initiator systems, especially hydroquinone/sulfonium salt mixtures. In particular, extensive studies were performed on MEHQ/triarylsulfonium salt systems. The effect of adding MEHQ to the system regarding cure speed, properties, and odor development were examined. In addition to MEHQ, other hydroquinone phenolic inhibitors such as  
10   toluhydroquinone and hydroquinone were evaluated but were not as desirable for some applications since they cause significant darkening of the solutions containing sulfonium salt initiator.

MEHQ added to sulfonium salt initiator solutions produced little to no color development during the time scale of the evaluation (seven months at room temperature),  
15   and, due to its solubility characteristics, is the easiest of the three additives tested to incorporate into the initiator solutions.

Moreover, addition of 1500 ppm or more of MEHQ (based on the total formulation) to the sulfonium salt initiator does not affect formulation cure speeds or cured properties.

20           Preferrably, the amount of deodorizing agent is comprised between 0.03% (300 ppm) and 0.4% (4000 ppm) by weight of the total formulation containing sulfonium salt initiator, polymerizable material and deodorizing agent. On these laboratory scales, MEHQ addition results in a noticeable improvement in the organosulfur/mercaptan/thio odor which develops during cure. Curing on a production scale will, of course, amplify

this deodorizing effect. Thus, addition of deodorizing agent MEHQ produces a unique and improved product which distinguishes the present invention's initiator composition from conventional initiators. In addition, since the odor reduction mechanism seems to be dependent on a sulfonium salt photoproduct/ MEHQ interaction, addition of MEHQ to the initiator package assures that the ratio of the sulfonium salt initiator to MEHQ will remain constant.

Although it is difficult to predict the amount of initiator that will be required for a particular application, most published starting point formulations recommend using between 2 and 5 % sulfonium salt initiator. The following table lists the amount of odor inhibitor which should be added to the initiator to achieve 500 ppm inhibitor in a finished formulation.

Table A: Amount Odor Inhibitor Required to Achieve 500 ppm in Total Formulation

Formulation % Initiator	% Inhibitor in Initiator	ppm Inhibitor in Formulation
0.5 %	10 %	500
1.0 %	5 %	500
2.0 %	2.5 %	500
5 %	1 %	500
10 %	0.5 %	500

Among the sulfonium salt initiators and inhibitors tested were MEHQ, hydroquinone and tolhydroquinone.

Triaryl sulfonium salt initiators tested include the following:

Initiator	Counterion	% solids	Solvent
Union Carbide UVI-6990	PF <sub>6</sub> <sup>-</sup>	50 %	Propylene Carbonate
3M FX-512	PF <sub>6</sub> <sup>-</sup>	60 %	$\gamma$ -Butyrolactone
UCB Uvacure 1590	PF <sub>6</sub> <sup>-</sup>	50 %	Propylene Carbonate
Union Carbide UVI-6974	SbF <sub>6</sub> <sup>-</sup>	50 %	Propylene Carbonate

Preferred solvents for the initiators are propylene carbonate or  $\gamma$ -butyrolactone.

Solubility of MEHQ/ Hydroquinone / Toluhydroquinone in Initiator Solutions:

MEHQ was found to be very soluble in initiator solutions, especially those containing propylene carbonate (Union Carbide and UCB initiators). Hydroquinone and toluhydroquinone are somewhat less soluble. However, all three additives are soluble at the level needed to impart odor reduction in a formulation (~ 6 % or less). FX-512 is a poorer solvent for the additives than UVI 6990, either because it uses a different solvent ( $\gamma$ -butyrolactone) or because of the higher solids content (60% for FX 512, versus 50 % in UVI 6990). Limited tests suggest that MEHQ inhibitor is equally soluble in Uvacure 1590 and in UVI 6990.

Table B: Amount of Additive Dissolved in Triarylsulfonium Salt Compositions

	Additive	Sulfonium Salt	% dissolved	time to dissolve
B1	MEHQ	UVI-6990	11.2 %	< 2 hours
B2	MEHQ	UVI-6990	32.6 % *	4 hours
B3	Toluhydroquinone	UVI 6990	9.7 % *	3 hours
B4	Hydroquinone	UVI 6990	8.1 % *	2 hours
B5	MEHQ	Uvacure 1590	6.4 % *	< 2 hours
B6	MEHQ	FX 512	9.6 % *	1 hours
B7	Toluhydroquinone	FX-512	11.1 % *	> 24 hours
B8	Hydroquinone	FX 512	10.0 % *	> 24 hours
B9	MEHQ	UVI-6974	11.5 % *	< 2 hours
B10	Toluhydroquinone	UVI 6974	8.7 % *	< 2 hours
B11	Hydroquinone	UVI-6974	8.9 % *	4 hours

\* Highest concentration tested.

Color Development in Initiator Solutions:



No color change was observed when 6 to 10 % MEHQ was added to UVI 6990, UVI 6974, Uvacure 1590 or FX 512. (The solutions were monitored for seven months at room temperature). Toluhydroquinone produced a noticeable color change when added to UVI 6990: the solution color deepened overnight and became more red. This is undesirable for many applications. When hydroquinone was added to the initiators, a similar effect occurred, although to a lesser extent than when toluhydroquinone was added.

Table C: Color Change in Initiator Solution on Addition of Additive

	Initiator	Additive	Amount added	Color after one week	Color Rank	Color after 7 months
C1	UVI 6990	None	0 %	light yellow	1	light yellow color
C2	FX 512	None	0 %	yellow	2	NT
C3	UVI 6990	MEHQ	3.6 %	light yellow	1	pale yellow
C4	UVI 6990	MEHQ	6.3 %	light yellow	1	pale yellow
C5	UVI 6990	MEHQ	11.2 %	light yellow	1	pale yellow, (some solids)
C6	UVI 6990	MEHQ	32.6 %	light yellow	NT	yellow (no solids)
C7	UVI 6990	MEHQ	6.4 %	light yellow	1	yellow
C8	UVI 6990	THQ	9.7 %	reddish	5	red-orange
C9	UVI 6990	HQ	8.1 %	medium reddish	4	dark orange
C10	FX 512	MEHQ	9.6 %	yellow color	2	dark yellow
C11	FX 512	THQ	11.1 %	medium reddish	4	dark orange, (some solids)
C12	FX 512	HQ	10.0 %	medium yellow	3	very dark orange (some solids)
C13	UVI 6974	MEHQ	11.5 %	light yellow	NT	yellow
C14	UVI 6974	THQ	8.7 %	NT	NT	red-orange
C15	UVI 6974	HQ	8.9 %	NT	NT	dark red

10 \* Relative color, 1 is lightest, 5 is darkest.

Presence of solids may be due to a number of factors. Precipitate can form in unmodified initiator solution, especially if exposed to moisture.

NT = no test

- Color development was not related to relative purity or initial color of the inhibitors used: HQ was in the form of pure white, needle-like crystals and THQ was in the form of a finely divided light colored powder. The MEHQ, in the form of 1 to 2 cm chunks with a definite tan to brown color, appeared less pure, but produced the least color in the initiator solutions.

Effect of Added MEHQ on Cure Speeds and Film Properties:

No significant effect on cure, either positive or negative, occurred with the addition of up to 1500 ppm MEHQ to the epoxide formulations evaluated.

A) Tests on Epoxy/Polyol Formulation:

- Two sets of panels were cured and evaluated to determine any trend in properties with regards to MEHQ content. All cured properties are within the margin of error of the tests.
- Tests were done using the following base formulation:

Component		% (Weight)
EEC	Cycloaliphatic epoxide	80.53 %
Union Carbide Tone 301	Polycaprolactone triol	18.95 %
Silwet L-7602	Surfactant	0.53 %
Initiator	Union Carbide UVI 6990	4.7-4.8 %
Viscosity: 346.0 cps @ 25 °C (4 spindle, 100 rpm)		

Four levels of MEHQ were tested at one initiator concentration:

% UVI 6990 *	ppm MEHQ
4.67	1560
4.77	951
4.72	510
4.81	0

\* Desired MEHQ level was achieved by adding unmodified UVI 6990 in combination with UVI 6990 containing 6.42 % MEHQ.

Run 1:

Experimental Conditions:

Substrate	Aluminum Q panel
Film Application:	# 5 wire wound rods (film thickness 0.35 mil / 9 micron)
Lamp:	One Fusion 300 watt/inch H bulb
Line Speed/ Dose:	90 fpm (27.4 m/min); 220 mJ/cm <sup>2</sup>
	45 fpm (13.7 m/min); 410 mJ/cm <sup>2</sup>
Temperature:	72 °F / 22 °C
Relative Humidity (%):	37

5 Table D: Results: Post-Cured Properties

			90 fpm*		45 fpm *	
	% UVI 6990 *	ppm MEHQ	MEK DR	Pencil Hardness	MEK DR	Pencil Hardness
D1	4.67	1560	52	2H	79	2H
D2	4.77	951	60	4H	83	4H
D3	4.72	510	56	4H	57	H
D4	4.81	0	49	4H	60	3H

\* Median of 2 to 4 panels each, surface was tack-free after 5 seconds for all compositions Cured film properties were measured after post cure at room temperature.

Run 2:

10 Experimental Conditions:

Substrate	Aluminum Q panel
Film Application:	# 5 wire wound rods (film thickness 0.35 mil / 9 micron)
Lamp:	One Fusion 300 watt/inch H bulb
Dose:	192 mJ/cm <sup>2</sup>
Line Speed:	100 fpm (30.5 m/min)
Temperature:	73 °F / 22.5 °C
Relative Humidity (%):	53

Table E: Results Cured Properties

	% UVI 6990 *	ppm MEHQ	One hour after Cure *		Post Cured **	
			MEK DR	Pencil Hardness	MEK DR	Pencil Hardness
E1	4.67	1560	15	F	22	4H
E2	4.77	951	17	B	14	6H
E3	4.72	510	17	B	20	6H
E4	4.81	0	15	F	20	4H

\* One panel.

\* Median of 3 panels.

Surface was tack-free after 5 seconds for all compositions. Post-cured film properties, as  
 5 reported on Tables D and E, were measured after post cure at room temperature in  
 ambient conditions.

#### B) Tests on Epoxy Only Formulation:

Following the tests of the epoxy/polyol formulations, formulations consisting of  
 only initiator (2.9-3.0 %), MEHQ and EEC were evaluated. No statistically significant  
 10 differences in cured properties or cure speeds were detected for any composition tested,  
 regardless of MEHQ level.

The following formulations were evaluated:

Monomer	Initiator	% Initiator	ppm MEHQ
EEC	UVI 6990	2.96	0
EEC	UVI 6990	2.96	510
EEC	UVI 6990	2.90	1006
EEC	Uvacure 1590	2.93	0
EEC	Uvacure 1590	2.95	512
EEC	Uvacure 1590	2.90	1012
EEC	UVI 6990	2.96	500
EEC	Uvacure 1590	2.97	500

## Experimental Conditions:

Substrate	Aluminum Q panel
Film Application:	# 5 wire wound rods (film thickness 0.35 mil / 9 micron)
Lamp:	One Fusion 300 watt/inch H bulb
Dose:	192 mJ/cm <sup>2</sup>
Line Speed:	30 fpm (30.5 m/min)
Temperature:	72 °F / 22 °C
Relative Humidity (%):	33

Table F: Results Cured Properties: For all compositions cured in this series, properties after post cure were identical:

	Initiator	% Initiator	Ppm MEHQ	Tack Free Time*	MEK DR	Pencil Hardness	Crosshatch Adhesion
F1	UVI 6990	2.96	0	20 s	200 +	4 H	< 5 %
F2	UVI 6990	2.96	510	25 s	200 +	4 H	< 5 %
F3	UVI 6990	2.90	1006	15 s	200 +	4 H	< 5 %
F4	Uvacure 1590	2.93	0	20 s	200 +	4 H	< 5 %
F5	Uvacure 1590	2.95	512	25 s	200 +	4 H	< 5 %
F6	Uvacure 1590	2.90	1012	15 s	200 +	4 H	< 5 %
F7	UVI 6990	2.96	500	20 s	200 +	4 H	< 5 %
F8	Uvacure 1590	2.97	500	20 s	200 +	4 H	< 5 %

5 \* Margin of error for tack-free time is ~ ± 5 seconds. Short tack-free times are better.

Effect of MEHQ on Odor Produced on Cure:

Testing proved that the addition of MEHQ reduces the organosulfur/mercaptan/thio odor which develops during cure. Curing on a larger (commercial) scale will amplify the odor reduction effect.

The following formulations were evaluated for the effect on odor after cure:

	Composition	Initiator	% Initiator	ppm MEHQ
1	EEC	UVI 6990	3.0	0
2	EEC	UVI 6990	3.0	0
3	EEC	UVI 6990	3.0	0
4	EEC	UVI 6990	3.0	0
5	Base formulation *	UVI 6990	4.8	0
6	Base formulation *	UVI 6990	4.8	0
7	Base formulation *	UVI 6990	4.8	500
8	EEC	UVI 6990	3.0	489
9	EEC	UVI 6990	2.9	1006
10	EEC	UVI 6990	3.0	510
11	Base formulation *	UVI 6990	4.8	0
12	EEC	UVI 6990	2.9	1006

\* Base formulation contained 76.5 parts EEC, 18 parts Tone 301, 0.5 parts Silwet L-7602.

#### Experimental Conditions:

Substrate	Aluminum Q panel
Film Application:	# 5 wire wound rods (film thickness 0.35 mil / 9 micron)
Lamp:	Fusion 300 watt/inch H bulb
Dose:	578 mJ/cm <sup>2</sup>
Temperature:	71 °F / 22 °C
Relative Humidity (%):	30

5

Panels were placed into plastic jars ~ 20 seconds after cure, the jars were sealed with tape, then placed in 60 °C oven overnight. The odor of two panels at a time were compared and ranked. In the majority of cases, addition of the quinone derivative reduced the odor of the cured panels.

10

Table G: Results: Odor of Cured Panels

Less Odor				More Odor			
	Composition	% Initiator	ppm MEHQ		Composition	% Initiator	ppm MEHQ
G1	EEC	3.0	0	<	Base formulation	4.8	0
G2	EEC	3.0	489	<	EEC	3.0	0
G3	EEC	3.0	510	<	EEC	3.0	0
G4	EEC	2.9	1006	<	Base formulation	4.8	0
G5	Base	4.8	0	≈	Base	4.8	500

	Less Odor				More Odor		
	Composition	% Initiator	ppm MEHQ		Composition	% Initiator	ppm MEHQ
	formulation				formulation		
G6	EEC	3.0	0	=	EEC	2.9	1006

A second set of panels were cured and tested to confirm the previous results.

Composition	Initiator	% Initiator	ppm MEHQ
EEC, surfactant *	Uvacure 1590	3.0	0
EEC, surfactant *	Uvacure 1590	2.9	512
EEC, surfactant *	Uvacure 1590	2.9	991
EEC, surfactant *	Uvacure 1590	2.9	2009

5

\* Composition was 99.5 parts EEC and 0.5 parts Silwet L-7602.

Experimental Conditions:

Substrate	Aluminum Q panel
Film Application:	# 5 wire wound rods (film thickness-0.35 mil / 9 micron)
Lamp:	Fusion 300 watt/inch H bulb
Dose:	260 mJ/cm <sup>2</sup>
Temperature:	70 °F / 21 °C
Relative Humidity (%):	50

Table H: Results: Odor of Cured Panels

	Less Odor			More Odor	
	% Initiator	ppm MEHQ		% Initiator	ppm MEHQ
H1	2.9	991	<	3.0	0
H2	2.9	2009	<	2.9	512

10

The relative odor of cured panels was quantified in the following trial. No odor is classified as 0, and strong odor is classified as 5. As before, only two panels were evaluated at a time.

Table I: Results: Quantify Odor of Cured Panels

	% Initiator	ppm MEHQ	odor	% Initiator	ppm MEHQ	odor
I1	3.0	512	1	3.0	0	5
I2	2.9	991	3	2.9	2009	2
I3	3.0	0	5	2.9	2009	1
I4	2.9	512	2	2.9	991	4

From the above detailed specification and examples, it can be seen that the photopolymerizable composition of the present invention reduces the undesirable organosulfur/mercaptan/thio odor generated from the decomposed sulfonium salt released upon curing of sulfonium salt photoinitiator systems.

The foregoing description and examples of the present invention are merely illustrative thereof, and it is understood that other embodiments, variations and modifications can be effected without departing from the spirit or scope of the invention as set forth in the following claims.



## Claims

1. A cationic initiator composition for initiating cationic polymerization comprising:  
5 a) a sulfur- or nitrogen-containing initiator and  
b) a deodorizing agent;  
wherein the deodorizing agent reduces the odor of the initiator composition upon initiation.
- 10 2. The composition of claim 1, wherein the initiator is a sulfonium salt.
3. The composition of claim 1, wherein cationic polymerization of the composition is initiated by a member selected from the group consisting of ultraviolet, visible light, infrared, microwaves, radio, alpha, beta, gamma, X-rays and electron beams.
- 15 4. The composition of claim 1, wherein the deodorizing agent is a free radical inhibitor or a phenolic compound.
5. The composition of claim 4, wherein the phenolic compound is a quinone or a quinone derivative.
- 20 6. The composition of claim 5, wherein the quinone derivative is selected from the group consisting of hydroquinone, toluhydroquinone and methylether of hydroquinone.
7. The composition of claim 6, wherein the quinone derivative is methylether of hydroquinone.
8. The composition of claim 3, wherein the initiator comprises an arylsulfonium salt  
25 or a phenacylsulfonium salt.
9. The composition of claim 8, wherein the arylsulfonium salt or phenacylsulfonium salt is selected from the group consisting of dialkylphenacylsulfonium salts, dialkyl-4-hydroxyphenylsulfonium salts, bis-p-diphenylsulfoniumphenylsulfide salts, diphenylphenylthiophenyl sulfonium salts, benzylsulfonium salts,

benzyltetramethylene sulfonium salts, benzyl(p-hydroxyphenyl)methyl-sulfonium salts, triarylsulfonium salts, triphenylsulfonium salts and mixtures thereof.

10. The composition of claim 6, wherein the initiator comprises an arylsulfonium salt or a phenacylsulfonium salt.
- 5 11. The composition of claim 10, wherein the arylsulfonium salt or phenacylsulfonium salt is selected from the group consisting of dialkylphenacylsulfonium salts, dialkyl-4-hydroxyphenylsulfonium salts, bis-p-diphenylsulfoniumphenylsulfide salts, diphenylphenylthiophenyl sulfonium salts, benzylsulfonium salts, benzyltetramethylene sulfonium salts, benzyl(p-hydroxyphenyl)methyl-sulfonium  
10 salts, triarylsulfonium salts, triphenylsulfonium salts and mixtures thereof.
12. The composition of claim 1 further comprising a solvent.
13. The composition of claim 12, wherein said solvent is selected from the group consisting of propylene carbonate,  $\gamma$ -butyrolactone, tetrahydrofuran, *N,N*-dimethylformamide, tetrahydropyran, aliphatic alcohols, aliphatic hydrocarbons,  
15 aromatic hydrocarbons, dioxane, dimethoxyethane, acetone, acetonitrile and mixtures thereof.
14. The composition of claim 13, wherein the solvent is propylene carbonate or  $\gamma$ -butyrolactone.
15. A curable cationic polymerizable composition comprising:
- 20 a) a sulfonium salt initiator,  
b) polymerizable material, and  
c) a deodorizing agent;  
wherein the deodorizing agent reduces the odor of the composition upon  
initiation.
- 25 16. In a process for curing a cationic polymerizable composition containing:  
a) a sulfonium salt initiator and  
b) polymerizable material;

the improvement which comprises adding a deodorizing agent to said composition in order to reduce the odor upon curing.

- 5 17. A photoresist composition comprising:  
a photoactive sulfonium salt,  
a resin binder and  
a deodorizing agent;  
wherein said deodorizing agent reduces the odor of the photoresist composition upon cure.
- 10 18. The photoresist composition of claim 17, wherein said composition is a chemically amplified positive-acting photoresist.
- 15 19. The photoresist composition of claim 17, wherein said composition is a negative-acting photoresist.
- 20 20. An article of manufacture having at least one surface, wherein said at least one surface comprises a coating layer of the photoresist composition of claim 17.
21. In a process for preparing a photoresist composition containing:  
a) a photoactive sulfonium salt and  
b) a resin binder;  
the improvement which comprises adding a deodorizing agent to said photoresist composition in order to reduce the odor upon curing.
- 25 22. The process of claim 21, wherein said photoresist composition is a chemically amplified positive-acting photoresist composition.
- 30 23. The process of claim 21, wherein said photoresist composition is a negative-acting photoresist composition.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 02/09248

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G59/68

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,Y	US 4 218 531 A (CARLSON ROBERT C) 19 August 1980 (1980-08-19) claims; examples ---	1-23
Y	DATABASE WPI Section Ch, Week 198826 Derwent Publications Ltd., London, GB; Class D22, AN 1988-179850 XP002197218 & JP 63 117763 A (NIPPON SHOKUBAI KAGAKU KOGYO CO LTD), 21 May 1988 (1988-05-21) abstract ---	1-23
X	US 4 250 203 A (KESTER DENNIS E ET AL) 10 February 1981 (1981-02-10) column 9, line 9 -column 13, line 15; claims; examples --- -/--	1-23



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents:

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- \*E\* earlier document but published on or after the international filing date
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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\*A\* document member of the same patent family

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## INTERNATIONAL SEARCH REPORT

International Application No  
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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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